

【Abstract】

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The present invention relates to networked silica produced by treating silanol groups with organic silane and combining silica particles with one another and the process thereof. When networked silica manufactured by the present invention is added to rubber compounds, the tensile strength and the elongation at break highly increase while the modulus of rubber compounds slightly increase. Networked silica has excellent dispersion property so that the reinforce effect shows highly in spite of a little addition. Moreover, it dose not absorb additives such as curative accelerators to enhance the economic efficiency of the rubber compounds.

【Representative drawing】

Fig 1.

【Specification】

【Title of the Invention】

NETWORKED SILICA FOR ENHANCING TENSIBLE STRENGTH OF RUBBER COMPOUND DRASTICALLY, AND THE PROCESS THEREOF

【Brief Description of the Drawings】

Fig. 1 is photos of the cut surface of the rubber compound reinforced with silica, showing the dispersibility difference of silica. Silica aggregates are not shown in rubber compound reinforced with networked silica so that silica is mixed ideally.

Fig. 2 is results of thermogravimetric analysis of silica modified by organic silane and networked silica.

Fig. 3 is infrared absorption spectrums of silica modified by organic silane, which shows that functional groups are coupled with silica.

Fig. 4 is infrared absorption spectrums of networked silica, which shows carbon chain is combined stably even though it is heated at high temperature.

【Description of the Invention】

【Purpose of the Invention】

【Field of the Invention and the Prior Art】

The present invention relates to networked silica for enhancing tensile strength of rubber compound drastically and the process thereof. More particularly, the present invention relates to networked silica having three-dimensionally connected bridge chains among silica particles produced by introducing a functional group on surface by

reacting silanol groups on surface of silica and alkoxyl silane having functional group and reacting that again or reacting a coupling reagent where diisocyanate, halogen atoms, or ester groups were combined at both ends of carbon chain and silica.

A rubber compound is deformed under a given stress, but is an elastic material recovering their own shape when the stress is released. The shock-absorbing function of rubber compounds makes it possible to be applied them to a variety of products such as tires, conveyers, belts, cords, earthquake-proof materials, and shoes. A double bond of a rubber molecule is bridged by sulfur during curing process so that the rubber compound enhances the elasticity. The maximum force required to break a rubber compound in tensile test shows tensile strength (T.S.) and the elongated ratio at the break point shows elongation at break (E.B.). If the elasticity is required, the crosslinking density is lowered to raise elongation at break, but if the tensile strength is required, the crosslinking density is raised to enhance the elasticity.

There is a limit to increasing the elasticity by raising the crosslinking density because a high crosslinking density of a rubber compound gives a high tensile strength, but a rubber compound becomes rigid and easily brittle. Therefore several types of fillers have been employed for rubber compounds. The properties such as elasticity of rubber are enhanced by addition of approximately 50phr of carbon black to a rubber compound for manufacturing tires. Recently, silica as well as carbon black has been added as fillers. Silica has high mechanical stability compared with carbon black so that the addition of silica improves the elasticity and mileage of cars is raised. Furthermore, silica is thermally and mechanically stable and is not emitted pollutants during driving so that it contributes to preventing the environmental pollution. An amount of silica added to rubber compounds as environmental benign filler having has increased.

Particularly, addition of silica to tread of tires enhance their rolling resistance and adherence on wet ground are enhanced. Since these two properties change in the opposite direction according to content of carbon black, typical reinforcing material, it is difficult to optimize these properties by adding only carbon black. However, addition of silica can enhance both properties so that a large part of content of carbon black is substituted by silica. Moreover, since silica is white contrary to carbon black, it is possible to adjust colors of rubber products and raise value added by introduction of colors so that an amount of using silica fillers has increased.

Although silica has many advantages as a reinforcing material as described above, it is difficult to increase content of silica because it is an inorganic material not to mix with a rubber compound, an organic compound. In order to maximize a reinforcing effect of elasticity, its particles should be individually dispersed in a rubber compound but rubber molecules are not easily miscible with silica due to large molecular size, low fluidity. For this reason, it is difficult to mix silica with rubber compounds and takes a long time. Extremely, physical properties of rubber compounds might be lowered by silica added for reinforcing elasticity.

In order to enhancing dispersion of silica, the surface of silica particles is coated with organic materials to make silica particles mixed with rubber compounds by affinity between organic materials. It is possible to enhance both dispersion and reinforcing ability because the coated organic material contains a functional group to couple with rubber compounds so that silica can couple with rubber compounds. For this purpose, coupling reagents containing two alkoxy silane functional groups at their terminals to react with silanol groups on the surface of silica and sulfide bonds between these groups are added to a rubber compound. When alkoxy silane group reacts with silanol groups

on the surface of silica, alcohol is produced, alkoxy group is removed, and silane is coupled with a polar group on the surface of silica. Coating of the surface of silica with organic materials improves affinity between a rubber compound and silica. When dissociated sulfide groups combine with double bonds of rubber molecules during curing, silica particles directly combine with rubber molecules by chemical bonds so that reinforcing effect is maximized. Furthermore, when silica particles combines with one another by a coupling reagent and rubber molecules are placed among them, the resistance to ruptures of rubber compounds becomes higher to increase the tensile strength highly.

However, currently, the coupling reagents are added during mixing of rubber compounds and the coupling reagents react with silica or rubber compounds during curing process. Therefore, the entire added coupling reagents don't react with silica or rubber compounds and content contributing to enhancing the tensile strength of rubber compound is not so high. Moreover, since the coupling reagents react with silica or rubber compounds by a variety of coupling method, there is a limit to effecting as coupling reagents. When silica directly combines with rubber compounds through bridges of coupling reagents, the tensile strength becomes higher, but also modulus of rubber compounds becomes higher and the function as elastic materials is lowered. During mixing, heat is generated and the temperature is elevated inevitably. When the temperature is higher than 170°C, organic silane coupling reagents are dissociated and sulfur radicals being capable of processing curing are produced. For this reason, rubber compounds with coupling reagents should be controlled below 170°C during mixing. Although coupling reagents are effective for enhancing the tensile strength, they also have a lot of disadvantages. Since addition of coupling reagents results in enhancing the

tensile strength of rubber compounds with silica and dispersion and improving the physical properties and safety from impact of rubber products, coupling reagents have been used in specific products requiring high tensile strength and high impact safety such as carcass, belt of tires although coupling reagents are expensive and have a lot of limitations to use.

Since a part of the added materials of tires are volatilized by heat generated during driving and minute particles are emitted by friction, it is important whether or not raw materials are harmful. It is encouraged to use silica which is chemically stable and harmless rather than carbon black with concern about emission of harm materials in rubber compounds of tires. The content of silica is increased in order to enhance mileage of cars and suppress not only materials emitted by tires but also emission of pollutants generated during driving, such as exhaust. Although increasing the content of silica is desirable in terms of reducing emission of pollutants, curative accelerators, activators, etc. are captured on polar groups of silica surface. In order to compensate for additives which are absorbed to lose functions, actually the content is adjusted highly. Since the cost of raw materials becomes higher by overuse of additives and environmental pollution is caused by emission of non-reacted additives, the chemical and physical properties should be controlled not to absorb another additives on silica.

In summary, when the content of silica increases to maximize the function of silica as fillers and minimized side effects, the effect of adding silica can be maximized. Particularly, lowering dispersion of silica caused by increasing the content of silica and increasing cost due to adjusting the content of curative accelerators and activators highly must be solved. Lowering dispersion due to increase in the content of silica lowers the tensile strength and elevation of modulus due to direct combination silica

with rubber compounds lowers impact absorption function of rubber products and might cause damage by impact. Although dispersion property of silica can be improved partially by use of coupling reagents, it is impossible to exclude completely losing activities of rubber additives and early cure due to dissociation thereof. These problems due to addition of silica lower performance of rubber products and elevate the cost so that they can offset positive effects.

【Technical problems of the present invention】

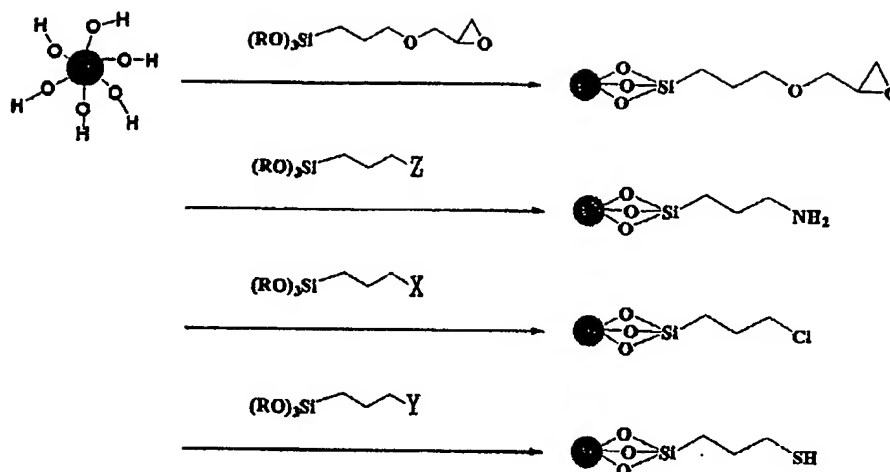
In spite of these problems, the loading amount of silica as fillers is increasing in terms of enhancing the tensile strength, giving functions such as colors and preventing environmental pollution and is expected to increase from now on. However, as described above, increase in content of silica can cause more serious problems due to use of silica fillers. For overcome these problems, the present invention provides networked silica for suppressing absorption of rubber additives such as an curative accelerator by surface silanol groups by means of reacting silica with organic materials and reducing polar groups, preventing increase in modulus by preventing direct combination rubber compounds with silica, and enhancing the tensile strength of rubber compounds by combining silica particles at proper intervals and entangling rubber compounds put among them with silica. Accompanying with this, the function as fillers is maximized by increasing affinity between organic materials coupled on the surface of silica and rubber compounds and enhancing dispersion of silica regarding to rubber compounds. The networked silica having three-dimensional network structure is manufactured in order to enhance positive effects and minimize negative effects of addition of silica. Rubber molecules intrude into openings formed among silica particles

and are entangled with silica particles three-dimensionally so that the tensile strength increases by addition of networked silica, while increase in their modulus is minimized because rubber molecules are not combined with silica directly. Moreover, since polar silanol groups on the surface of silica are removed by reaction with silane so that curative accelerators or activators are not absorbed on networked silica, there is no need of adding curative accelerators or activators excessively in site of adding a lot of networked silica. Addition of networked silica having network structure by combining silica particles through carbon chain at proper intervals results in enhancing physical properties such as tensile strength while it does not cause high increase in modulus. Although when using silica, content of additives must be increased, when using networked silica, additives such as curative accelerators are not absorbed because most of polar functional groups react with silane and are shielded so that it is possible to reduce the cost of additives and contribute to preventing environmental pollution by minimizing emission of harm materials.

【Construction and Effect of the Present Invention】

There are a lot of silanol groups on the surface of silica in spite of varying with types. Although their chemical properties are different from weak acid silanol groups to approximate neutral silanol groups, most of them on the surface of silica easily react with alkoxyl silane so that silane can be coupled on the surface of silica as shown in following reaction formula.

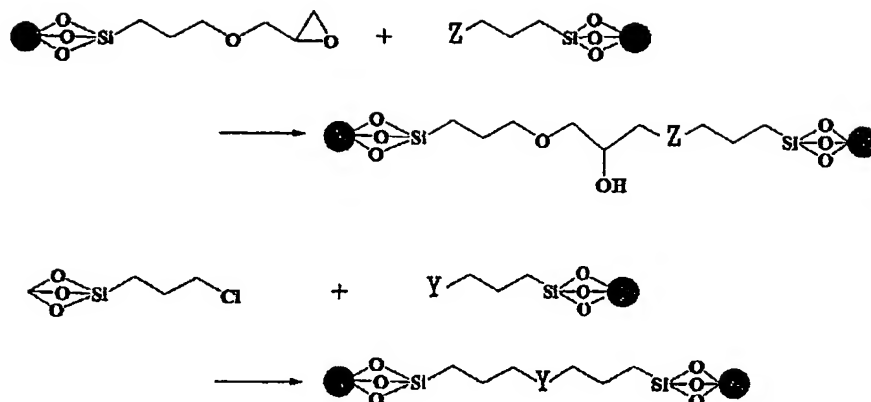
[Reaction Scheme 1]



(In above reaction formula, spheres show silica particles, Z shows amine, imine or isocyanate groups, X shows halogen atoms, and Y shows thiols or hydroxy groups)

Methanol in methoxy silane and ethanol in ethoxy silane are produced and silane is coupled with silica. Since alkoxy silane having epoxy groups at the opposite of alkoxy groups can be combined with materials having amine or imine groups, silica particles can be combined at a certain intervals by combining silica having epoxy groups with silica having amine or imine groups as shown in reaction formula 2. In addition to silane having epoxy and amine groups, silane having halogen atoms, thiols or hydroxy groups can be combined with silica particles.

[Reaction Scheme 2]



Networked silica shown in reaction formula 3 is produced by reaction of silica coupled with silane with one another to combine three-dimensionally.

(In above reaction formula, A and B show combinable functional groups, n and m show reaction ratio of silane-coupled silica.)

Organic functional groups coupled with silanol groups react with one another and silica particles are connected through organic bonds. Polar groups on the surface of silica are removed by reaction with silane and silica particles are combined with one another. The density of bridge chains of networked silica and the average distance between silica particles can be controlled by controlling the length of carbon chains of organic materials combined with silane and a coupling amount of silica. Halogen atoms include fluorine, chlorine, bromine atoms and chlorine atom is preferred.

Surface of networked silica is covered with organic materials and silica can be mixed with rubber compounds to enhance dispersion property highly. Moreover, dissolved rubber molecules intrude into openings of networked silica and are ideally entangled with silica particles to maximize of silica. Since rubber molecules are not directly combined with silica to enhance the tensile strength, not to increase modulus, silica has excellent performance as fillers for enhancing tensile strength of rubber

compounds. Compared with coupling reagents reacting with silica during curing reaction, when networked silica which is bridged beforehand is mixed with rubber compounds, an loading amount of silane becomes small because all of added silane is combined with silica so that desired reinforcing effect can be achieved with a small loading amount and manufacturing cost can be reduced. Moreover, there is an advantage that additives such as curative accelerators or activators for compensating the loss due to absorption of additives on the surface of silica do not need to be added excessively. The cost reduction of additives can lower manufacturing cost of rubber compounds and prevent environmental pollution due to emission of non-reacted additives during driving.

Functional groups as described above are exemplary and it is not limited to them.

The present invention is further described with examples. However, the scope of the invention is not limited by the examples.

Example 1.

After dissolving 24g of 3-glycidyloxypropyltriethoxy silane (gPTS) in 500ml of toluene in round-bottomed flask, 50g of silica with a large amount of silanol groups (Rhodia Zeosil 175) was added. Silane reacted with silanol groups on the surface of silica by connecting efflux heater and heating at 110°C for 24 hours. After cooling and washing with toluene, coupled silica was dried at 100°C for 12 hours. In the same method, silica coupled with 3-amiopropyltriethoxy silane (APTS), 3-mercaptopropyltriethoxy silane (MPTS), 3-chlororophyltriethoxy silane (CPTS) were prepared. Silica coupled with silane was written as GPTS-SIL, APTS-SIL, MPTS-SIL

and CPTS-SIL according to silane being coupled. Coupled amount of silane was determined by thermogravimetric analysis based on the weight loss due to the combustion of carbon and hydrogen of silane with air at elevated temperature. Coupled amounts of organic materials in silane coupled on silica were 1.2mmol/g, 1.5mmol/g, 0.7mmol/g and 0.5mmol/g in GPTS-SIL, APTS-SIL, MPTS-SIL and CPTS-SIL, respectively.

Epoxy groups reacted with amine groups to be combined. 100g of networked silica were produced by a reaction of 50g of GPTS-SIL with 50g of APTS-SIL in toluene. Also, it was produced by reactions of MPTS-SIL with GPTS-SIL or APTS-SIL with GPTS-SIL. When GPTS-SIL reacted with CPTS-SIL, HCl was removed and a covalent bond was produced to combine silica particles with one another.

Fig. 2 shows results of thermogravimetric analysis of silica modified by organic silane and networked silica. In silica, water was desorbed around 100°C and additional weight loss was not observed despite increase in temperature. However, in GPTS-SIL modified by organic silane, the weight loss was observed around 250°C and in networked silica, the range of weight loss was large. Since it was drawn in airflow and it showed weight loss by combustion of organic materials, coupling amount of organic materials was determined by this result.

Networked silica was produced by using n-hexane diamine having amine groups combined at both ends of carbon chains. A reaction of GPTS-SIL with n-hexane diamine caused a reaction of epoxy groups with amine groups to form a covalent bond. Since amine groups at both ends of n-hexane diamine reacted with epoxy groups coupled on another silica particles, networked silica with long carbon chain was produced.

Networked silica was produced by a reaction of diisocyanate having isocyanate at both ends of carbon chain with silica not to be modified by silane. Since isocyanate groups were directly combined with silanol groups on silica, they could produce networked silica through just one step. In the same method, networked silica could be produced by using hydrocarbon having chlorines at both ends. Instead, they required high temperature or long reaction time because of low reactivity.

In combining silane and manufacturing networked silica, a coupling amount and a state of coupling can be determined by thermogravimetric analysis and IR spectroscopy, respectively.

Fig. 3 shows IR absorption spectrums of silica coupled with silane. It showed the properties of silica produced by a reaction of epoxy groups, amine, chlorine, isocyanate as coupling reagent with silanol groups on silica. Absorption band of carbohydrate in $2,800\sim 3,100\text{cm}^{-1}$ frequency was shown. Simultaneously, absorption bands of specific functional groups such as amine, carbonyl groups were shown. These absorption bands were stable within 200°C in spite of having differences according to materials. IR absorption spectrums of networked silica produced by reactions of GPTS-SIL with APTS-SIL and GPTS-SIL with MPTS-SIL are shown in Fig. 3. Although the absorption bands became weak because functional groups reacted with one another, the absorption band of carbon chain, absorption band of $2,800\sim 3,100\text{cm}^{-1}$ remained to show proper coupling. Moreover, since the absorption band of carbon chain still remained in case of heating at 300°C with refluxing and silane reacted with one another to be combined, it confirmed the generation of considerably stable networked silica. Networked silica coupled with diisocyanate, chloride and ester groups showed similar results. However, dissociation was observed around 200°C because of a little lower

thermal stability.

Example 2.

The reinforcing performance of networked silica was analogized from changes in physical properties investigated after mixing in rubber compound and curing. Rubber compounds were mixed in an internal mixer. After masticating solution-polymerized styrene-butadiene rubber (S-SBR) for one minute, silica, coupling reagent, aromatic oil were added and were masticated for three minutes. After adding zinc oxide and stearic acid and masticating it three minutes, a primary master batches were obtained by pulling out rubber compounds 150~160°C. The second mixing processed below 110°C. After masticating the primary master batches for one minute, sulfur and curative accelerator were added. After masticating it for three minutes, rubber compounds were obtained. The compositions of four rubber compounds shown in Table 1. were the same except the contents of silica, coupling reagent, networked silica. R I -1 rubber compound did not contain silica, R I -2 rubber compound contained only silica, R I -3 rubber compound contained both silica and coupling reagent and R I -4 rubber compound contained only networked silica except both silica and coupling reagent. In mixed S-SBR, the glass transition temperature was -42°C, average molecular weight was 560,000 and the contents of styrene and vinyl groups were 31% and 30%, respectively.

Table 1 shows results of tensile strength test of rubber compounds mixed with N-GA(1.0)-SIL networked silica produced by a reaction of GPTS(1.0)SIL with APTS(1.0)-SIL. A sample sheet for physical properties test was prepared by putting rubber compounds into a conventional flat-type mold and curing them by high pressure press at 160°C. In name of networked silica, N denoted networked, g and A denoted an

initial letter of an abbreviation of silane and numbers in parenthesis denoted nmol number of silane coupled per gram. Namely, N-GA(1.0)-SIL networked silica is a networked silica produced by a reaction of silica coupled with GPTS of 1.0mmol/g with silica coupled with APTS of 1.0mmol/g.

Table 1. Comparison of physical properties of rubber compounds according to addition of silica.

| Rubber compound | RI-1 | RI-2 | RI-3 | RI-4 |
|--------------------------------|-------|-------|-------|-------|
| Composition (phr) | | | | |
| Rubber ^a | 137.5 | 137.5 | 137.5 | 137.5 |
| Zinc oxide | 4.0 | 4.0 | 4.0 | 4.0 |
| Sulfur | 1.5 | 1.5 | 1.5 | 1.5 |
| Accelerator ^b (CZ) | 1.5 | 1.5 | 1.5 | 1.5 |
| Accelerator ^c (DPG) | 1.0 | 1.0 | 1.0 | 1.0 |
| Stearic acid | 2.0 | 2.0 | 2.0 | 2.0 |
| Silica ^d | – | 13.0 | 13.0 | – |
| Coupling reagent ^e | – | – | 1.0 | – |
| Networked silica ^f | – | – | – | 13.0 |
| Cure characteristics | | | | |
| Max. torque (lb·in) | 18.4 | 22.5 | 22.9 | 20.3 |
| Mini. Torque (lb·in) | 5.9 | 7.8 | 7.2 | 8.9 |
| t ₄₀ (min) | 8.7 | 11.2 | 9.1 | 1.5 |
| T ₉₀ (min) | 10.7 | 12.9 | 10.9 | 4.8 |
| Processibility | | | | |
| Mooney viscosity (lb·in) | 34.0 | 42.0 | 41.0 | 74.0 |
| T ₀₅ (분) | 40.0 | 59.0 | 47.0 | 2.7 |
| T ₃₅ (분) | 52.0 | 72.0 | 60.0 | 4.7 |
| Tensile property | | | | |
| Hardness (JIS A) | 29.0 | 36.0 | 37.0 | 40.0 |
| Modulus (kg/cm ²) | | | | |
| 100% | 6.4 | 7.7 | 8.7 | 7.8 |

| | | | | |
|--|-------|-------|-------|-------|
| 300% | - | 16.8 | 25.6 | 22.8 |
| Tensile strength (kg/cm ²) | 11.6 | 21.2 | 27.4 | 62.3 |
| Elongation at break (%) | 267.0 | 372.0 | 316.0 | 531.0 |
| Abrasion property PICO (g) | 1.26 | 0.17 | 0.15 | 0.14 |

In above Table,

^a : solution-polymerized SBR(oil-extended S-SBR polymer, content of oil is 37.5 phr)

^b : CZ (N-cyclohexyl-2-benzothiazol sulfenamide)

^c : DPG (N, N-diphenylguanidine)

^d : Zeosil 175

^e : si-69(Bis(triethoxysilyl propyl)tetra sulfane : TESPT)

^f : N-GA(1.0)-SIL

The tensile strength of the R I -1 rubber compound containing no silica was 11.6kg/cm², while the tensile strength of the R I -2 rubber compound containing 13 phr of silica was reinforced to 21.2kg/cm². Elongation at break also increased to 372% to show the reinforcing performance according to silica. When coupling reagent was added to silica, the reinforcing performance was enhanced. The tensile strength was enhanced to 27.4kg/cm². However, the 300% modulus increased to 25.6kg/cm² compared with 16.8kg/cm² when only silica was added and elongation at break decreased to 316% compared with 372% to show deterioration of elasticity. Compared with this, adding networked silica caused a little increase in 300% modulus to 22.8kg/cm² from 16.8kg/cm² of R I -2 rubber compound containing silica while it caused a high increase in the tensile strength to 21.2kg/cm² from 62.32kg/cm². Although the tensile strength of R I -3 rubber compound containing silica and coupling reagent was 27.4kg/cm², the

tensile strength of R I -4 rubber compound was up to two times higher than that of R I -3 rubber compound. Since elongation at break was high, 538%, the elasticity was maintained in spite of high increase in the tensile strength so that networked silica was a good reinforcing material for enhancing both tensile strength and elongation at break.

In addition to physical properties, abrasion property was highly enhanced in rubber compound containing networked silica as in the rubber compound containing silica. The positive effect due to addition of silica was maintained and the negative effect such as increase in modulus was not significant relatively.

Example 3.

Since the reinforcing effect of silica depended on loading amounts of silica and coupling reagent, the tensile strength of rubber compound varying with species and loading amounts of silica were examined and shown in Table 2. Silica was Zeosil 175, N-GA(1.0)-SIL was networked silica produced by GPTS(1.0)-SIL and APTS(1.0)-SIL and N-GM(1.0)-SIL was produced by GPTS(1.0)-SIL and MPTS-SIL. Rubber compounds were prepared by controlling loading amounts of silica regarding to SBR rubber to be 10phr, 20phr and 40phr. Since contents of zinc oxide, sulfur, curative accelerators, stearic acid were fixed as in Table 1, these additives were totally denoted as "Additive group 1"

Table 2. Change in physical properties of SBR compound according to loading amount of networked silica.

| Rubber compound | R II-1 | R II-2 | R II-3 | R II-4 | R II-5 | R II-6 | R II-7 |
|-------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Composition(phr) | | | | | | | |
| Rubber ^a | 137.5 | 137.5 | 137.5 | 137.5 | 137.5 | 137.5 | 137.5 |
| Additive group 1 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Silica | - | 10.0 | 20.0 | 40.0 | - | - | - |
| Networked Silica ^b | - | - | - | - | 10.0 | 20.0 | 40.0 |
| Cure characteristics | | | | | | | |
| Max. torque(lb·in) | 17.7 | 19.7 | 22.7 | 30.6 | 19.1 | 21.5 | 28.9 |
| Mini. Torque(lb·in) | 5.1 | 5.8 | 7.2 | 13.3 | 5.8 | 7.5 | 10.8 |
| t ₄₀ (min) | 9.9 | 10.5 | 11.9 | 11.5 | 3.6 | 2.1 | 3.9 |
| t ₉₀ (min) | 12.3 | 12.3 | 15.4 | 34.2 | 5.6 | 7.0 | 24.8 |
| Processibility | | | | | | | |
| Mooney | | | | | | | |
| viscosity (lb·in) | 30.1 | 34.5 | 42.3 | 63.5 | 35.0 | 42.1 | 58.9 |
| t ₀₅ (min) | 40.7 | 50.4 | 65.5 | 58.3 | 15.1 | 5.7 | 4.7 |
| t ₃₅ (min) | 54.4 | 63.3 | 82.7 | 79.7 | 18.7 | 8.1 | 10.3 |
| Tensile property | | | | | | | |
| Hardness (JIS A) | 31.0 | 32.0 | 37.0 | 51.0 | 34.0 | 39.0 | 50.0 |
| Modulus (kg/㎠) | | | | | | | |
| 100% | 4.7 | 5.6 | 7.5 | 11.0 | 7.4 | 8.6 | 14.0 |
| 300% | 10.0 | 13.0 | 17.0 | 27.0 | 23.0 | 24.0 | 44.0 |
| Tensile strength | | | | | | | |
| (kg/㎠) | 10.9 | 24.5 | 40.3 | 108.0 | 38.9 | 82.4 | 181.0 |
| Elongation at break | | | | | | | |
| (%) | 329.0 | 471.0 | 549.0 | 751.0 | 431.0 | 630.0 | 699.0 |
| Abrasion property | | | | | | | |
| PICO(g) | 1.028 | 0.277 | 0.121 | 0.081 | 0.260 | 0.106 | 0.065 |

In above table,

^a : solution-polymerized SBR

^b : N-GA(1.0)-SIL

Addition of silica enhanced the tensile strength of rubber compounds and the range of increase in the tensile strength changed in proportion to a loading amount of silica. Although the tensile strength of R II-1 rubber compound was 10.94kg/cm², adding 10phr, 20phr and 40phr of silica resulted in increasing to 24.5kg/cm², 40.3kg/cm² and 108 kg/cm², respectively. The elongation at break also increased and the elasticity of rubber compound was enhanced by addition of silica. The increase in the tensile strength was considerable when adding networked silica rather than silica without surface treatment. Adding 10 phr, 20 phr and 40 phr of N-GA(1.0)-SIL reinforced the tensile strength to 38.9kg/cm², 82.4kg/cm² and 181kg/cm². Adding networked silica reinforced the tensile strength approximately twice than silica. The elongation at break also increased and networked silica had a good elasticity reinforcing effect.

Although addition of networked silica caused increase in tensile strength, no considerable change in modulus. The tensile strength of the rubber compounds without silica was too low to compare so that 100% modulus of the rubber compound containing silica was compared with that of the rubber compound containing networked silica. 100% modulus of R II-2, R II-3 and R II-4 rubber compounds containing silica were 5.6kg/cm², 7.5kg/cm² and 11kg/cm² and increased depending on a loading amount of silica. Although 100% modulus increased to 7.4kg/cm², 8.6kg/cm² and 14kg/cm² in R II-5, R II-6 and R II-7 rubber compounds containing networked silica, the range of increase in modulus was not high respectively compared with the tensile strength increasing approximately two times. Since addition of networked silica resulted in a little increase in modulus and high increase in the tensile strength, toughness was

improved highly and elasticity increased greatly.

Addition of networked silica also reinforced abrasion property highly. Although the degree of abrasion denoted as PICO was 1.028g in R II -1 rubber compound, it was lowered to 0.081g in rubber compound containing 40phr of silica. The PICO value in rubber compound containing 40phr of networked silica was lowered to 0.065g and the improvement of abrasion property by adding networked silica was considerable.

Example 4.

The function as networked silica might be slightly different dependent on the types of bridge chains. The tensile property of rubber compound containing N-GA(1.0)-SIL and N-GM(1.0)-SIL was compared with that of rubber compound containing silica and coupling reagent. N-GM(1.0)-SIL were networked silica produced by a reaction of GPTS-SIL with MPTS-SIL. In rubber compound with silica rather than that without silica, the tensile strength increased and in rubber compound with silica and coupling reagent, the tensile strength increased highly. The increase in the tensile strength by the addition of networked silica were higher so that the tensile strength and the elongation at break in rubber compound reinforced with networked silica were higher than that in rubber compound containing silica and coupling reagent.

The reinforcing effects were different dependent on the types of bridge chains. The tensile strength of RIII-5 rubber compound reinforced with N-GM(1.0)-SIL networked silica where GPTS and MPTS were coupled was slightly lower than that of RIII-4 rubber compound reinforced with N-GA(1.0)-SIL networked where GPTS and APTS were coupled. The tensile strength of RIII-4 and RIII-5 rubber compounds reinforced with networked silica were higher than that of RIII-3 rubber compound

reinforced with silica and coupling reagent. Since the content of bridge chains was similar one another, the increase in the tensile strength by the addition of them was explained by the difference of chemical properties of bridge chains. Since the tensile strength and modulus of the rubber compound with N-GM(1.0)-SIL networked silica having -C-S-O- bonds were higher than that of the rubber compound reinforced with N-GA(1.0)-SIL networked silica having -C-N-O- bonds, it was possible that a part of -C-S- bonds dissociated during mixing and curing were coupled with rubber. It was supported by the low elongation at break of the rubber compound reinforced with N-GM(1.0)-SIL networked silica.

Table 3. Effect of the type of bridge chains of networked silica on physical properties.

| Rubber compound | RIII-1 | RIII-2 | RIII-3 | RIII-4 | RIII-5 |
|--|--------|--------|--------|-------------------|-------------------|
| Composition (phr) | | | | | |
| Rubber ^a | 137.5 | 137.5 | 137.5 | 137.5 | 137.5 |
| Additive group 1 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Silica | - | 40.0 | 40.0 | - | - |
| Coupling reagent ^b | - | - | 3.2 | - | - |
| Networked silica | - | - | - | 40.0 ^c | 40.0 ^d |
| Cure characteristics | | | | | |
| Max. torque(lb-in) | 17.7 | 30.6 | 32.5 | 28.9 | 28.6 |
| Mini. Torque (lb-in) | 5.1 | 13.3 | 9.4 | 10.8 | 11.3 |
| t ₄₀ (min) | 9.9 | 11.5 | 11.9 | 3.9 | 3.1 |
| t ₉₀ (min) | 12.3 | 34.2 | 16.8 | 24.8 | 16.0 |
| Processibility | | | | | |
| Mooney | 30.1 | 63.5 | 50.2 | 58.9 | 56.3 |
| Viscosity (lb-in) | | | | | |
| t ₀₅ (min) | 40.7 | 58.3 | 71.1 | 4.7 | 9.1 |
| t ₃₅ (min) | 54.4 | 79.7 | 92.1 | 10.3 | 13.5 |
| Tensile property | | | | | |
| Hardness (JIS A) | 31.0 | 51.0 | 52.0 | 50.0 | 52.0 |
| Modulus (kg/cm ²) | | | | | |
| 100% | 4.7 | 11.0 | 16.0 | 14.0 | 16.0 |
| 300% | 10.0 | 27.0 | 54.0 | 44.0 | 51.0 |
| Tensile strength (kg/cm ²) | | | | | |
| 10.9 | 108.0 | 137.0 | 181.0 | 149.0 | |
| Elongation (%) | 329.0 | 751.0 | 540.0 | 699.0 | 600.0 |
| Abrasion property | | | | | |
| PICO(g) | 1.028 | 0.081 | 0.053 | 0.065 | 0.066 |

^a : solution-polymerized SBR

^b : si-69

^c : N-GA(1.0)-SIL

^d: N-GM(1.0)-SIL

Example 5.

The reinforcing function of networked silica might depend on an amount of bridge chains. Small amount of bridge chains resulted in small amount of carbon chains entangled with rubber molecules to show small reinforcing effect, while large amount of bridge chains resulted in large amount of carbon chains entangled with rubber molecules to show large reinforcing effect. However, excessive amount of bridge chains suppressed intrusion of rubber molecules and reinforcing effect might be reduced. The property reinforcing functions of N-GM-SIL varying with the content of bridge chains were compared in Table 4. The increases in physical properties by addition of networked silica were considerable, regardless of the content of bridge chains. While the tensile strength of the rubber compound reinforced with silica (RIV-2) was 110kg/cm^2 , that of the rubber compound reinforced with N-GM-SIL networked silica was about 150kg/cm^2 , regardless of an amount of bridge chains. Since the effects for enhancing the tensile strength were similar although the amount of bridge chains changed to 0.2mmol/g , 0.5mmol/g and 1.0mmol/g , it showed that approximate $0.2\sim 0.5\text{mmol/g}$ of bridge chains were sufficient for reinforcing effect of physical properties. In aspect of reinforcing effect, it was desirable that the openings among silica particles were sufficient for intrusion of long rubber molecules and the amount of bridge chains was not large in order to entangle them.

Table 4. Effect of an amount of bridge chains of networked silica on the physical properties.

| Rubber compound ㄱ | RIV-1 | RIV-2 | RIV-3 | RIV-4 | RIV-5 |
|--|---|--------|-------|-------|-------|
| Composition (phr) | | | | | |
| Rubber ^a | 137.5 | 137.5 | 137.5 | 137.5 | 137.5 |
| Additive group 1 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Silica | 40.0 | 40.0 | - | - | - |
| Coupling regeant ^b | - | 3.2 | - | - | - |
| Networked silica | - | - | 40.0 | 40.0 | 40.0 |
| *kind of networked silica | N-GM(0.2)-SIL N-GM(0.5)-SIL N-GM(1.0)-SIL | | | | |
| Cure property | | | | | |
| Max. torque(lb·in) | 33.9 | 24.1 | 31.9 | 30.5 | 28.6 |
| Mini. Torque(lb·in) | 17.4 | 12.4 | 13.0 | 13.2 | 11.3 |
| t ₄₀ (min) | 10.3 | 10.8 | 5.9 | 2.8 | 3.1 |
| t ₉₀ (min) | 26.0 | 14.2 | 8.8 | 7.9 | 16.0 |
| Processibility | | | | | |
| Mooney | - | - | - | - | 56.3 |
| Viscosity (lb·in) | - | - | - | - | 9.1 |
| t ₀₅ (min) | - | - | - | - | 13.5 |
| t ₃₅ (min) | - | - | - | - | |
| Tensile strength | | | | | |
| Harness (JIS A) | 51.0 | 52.0 | 50.0 | 51.0 | 52.0 |
| Modulus (kg/cm ²) | | | | | |
| 100% | 11.0 | 15.1 | 12.0 | 12.0 | 16.0 |
| 300% | 25.7 | 54.2 | 36.4 | 40.0 | 51.0 |
| Tensile strength (kg/cm ²) | | | | | |
| | 102.0 | 110.0 | 157.0 | 169.0 | 149.0 |
| Elongation (%) | 752.0 | 463.0 | 698.0 | 688.0 | 600.0 |
| Abrasion | | | | | |
| PICO (g) | 0.071 | 0.0515 | 0.059 | 0.056 | 0.066 |

Example 6.

Silica must be dispersed in rubber compounds in order to perform function as reinforcing materials. Since silica aggregates caused lowering the physical properties of rubber compounds, the dispersion of silica must be improved by masticating rubber compounds.

However, in networked silica, the surface of silica was covered with organic materials and particles are located at constant intervals so that the dispersion of silica was excellent. Fig. 1 is photos of RIII-2, RIII-3 and RIII-4 rubber compounds described in Table 3. Since silica in rubber compounds were shown as white spots ascribed by silica aggregates, the states of dispersion of silica were easily compared. In spite of mixing in the same condition as the method in Example 1, the states of dispersion of silica were considerably different. In the RIII-2 rubber compound, the size and the amount of silica particles were considerably large. Although in the RIII-3 rubber compound containing si-69 coupling reagent, silica particles were reduced to enhance the dispersion property, silica were still aggregated. On the other hand, in the RIII-4 rubber compound reinforced with N-GA(1.0)-SIL networked silica, silica particles were not observed. Silica was dispersed as particles as expected so that the silica aggregates were not observed. The dispersion property of silica was excellent regardless of type or amount of bridge chains in rubber compounds reinforced with networked silica as shown in these photos.

Example 7.

Although tires, typical rubber products have excellent absorption capability of given impacts as elastic materials, the physical properties of rubber compounds are

lowered by heat generated during driving. Exposure of rubber compounds to high temperature for a long time causes breakage of carbon chains due to thermal aging, resulting in decrease in the tensile strength and deterioration of stability for impact. Simultaneously, crosslinking may be processed partially by heat increases modulus of rubber compounds so that the rubber compounds become rigid and lose their elasticity. Although the addition of networked silica causes considerable increase in the tensile strength, the deterioration of physical properties by heat is too high so that it cannot be applied to products generating heat during use such as tires. Therefore, the change in physical properties due to thermal aging should be examined. Table 5 listed the examination results of changes in physical properties of rubber compounds reinforced with networked silica after thermal aging. For comparison, the properties of rubber compounds with silica and those of rubber compounds containing silica and coupling reagents were listed. Since the composition of rubber compounds was the same as that in Table 4, the description was omitted.

In general, the rubber compounds are rigid after thermal aging to increase modulus and decrease the tensile strength. These results were shown in Table 5 and the modulus increased and the tensile strength decreased after thermal aging regardless of the type of fillers. However, all of the rubber compounds showed the similar ratio of decrease in the tensile strength. Consequently, the rubber compounds with networked silica had excellent physical properties after thermal aging as well as the initial physical properties. While the tensile strength of the rubber compound with silica and coupling reagent (RIV-2) after thermal aging was 97kg/cm^2 , that of the rubber compounds reinforced with networked silica (RIV-3, RIV-4 and RIV-5) were above 140kg/cm^2 . The elongation at break of the rubber compounds reinforced with networked silica after

thermal aging was above 500% so that networked silica excellently functioned as reinforcing materials of rubber regardless of thermal aging.

Table 5. Physical properties after thermal aging of the rubber compounds reinforced with N-GM(1.0)-SIL.

| Rubber compound | RV-1 | RV-2 | RV-3 | RV-4 | RV-5 |
|--|-------|-------|---------------|---------------|---------------|
| *Kind of networked silica | - | - | N-GM(0.2)-SIL | N-GM(0.5)-SIL | N-GM(1.0)-SIL |
| Before thermal aging | | | | | |
| Tensile property | | | | | |
| Hardness (JIS A) | 52.0 | 52.0 | 50.0 | 51.0 | 52.0 |
| Modulus (kg/cm ²) | | | | | |
| 100% | 10.8 | 15.1 | 11.6 | 12.2 | 15.9 |
| 300% | 25.7 | 54.2 | 36.4 | 40.0 | 51.3 |
| Thermal strength (kg/cm ²) | | | | | |
| | 102.0 | 110.0 | 157.0 | 169.0 | 149.0 |
| Elongation (%) | 752.0 | 463.0 | 698.0 | 688.0 | 601.0 |
| After thermal aging | | | | | |
| Tensile property | | | | | |
| Hardness (JIS A) | 56.0 | 55.0 | 53.0 | 54.0 | 55.0 |
| Modulus (kg/cm ²) | | | | | |
| 100% | 13.7 | 17.6 | 14.9 | 16.6 | 17.7 |
| 300% | 33.9 | 60.9 | 44.7 | 53.9 | 63.4 |
| Tensile strength (kg/cm ²) | | | | | |
| | 98.0 | 97.0 | 140.0 | 145.0 | 149.0 |

Example 8.

In addition to SBR compound, the effects of addition of networked silica with respect to natural rubber (NR) used in tread of tires and belts. Table 6 listed the comparison of tensile properties of SBR compound and NR compound reinforced with networked silica. For comparison, tensile properties of rubber compounds with silica and rubber compounds with silica and coupling reagent were also listed.

SBR compound reinforced with networked silica caused high tensile strength and elongation at break compared with the rubber compounds containing silica and coupling reagents. The tensile strength of NR compound reinforced with networked silica was higher than that of the rubber compounds containing silica and coupling reagents although the degree of enhancement was small compared with that of SBR compounds.

Table 6. Tensile properties of SBR and NR compounds reinforced with networked silica.

| Rubber compound | RV-1 | RV-2 | RV-3 | RV-4 | RV-5 | RV-5 |
|-------------------------------|-------|-------|--------|-------|-------|--------|
| Composition (phr) | | | | | | |
| S-SBR ^a | 137.5 | 137.5 | 137.5 | | | |
| NR ^b | | | | 100.0 | 100.0 | 100.0 |
| Additive group 1 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Silica | 50.0 | 50.0 | - | 50.0 | 50.0 | |
| Coupling reagent | - | 4.0 | - | - | 4.0 | - |
| networked silica ^c | - | - | 50.0 | - | - | 50.0 |
| Cure property | | | | | | |
| Max. torque (lb-in) | 37.90 | 37.00 | 35.00 | 60.10 | 47.10 | 43.00 |
| Mini. Torque (lb-in) | 19.90 | 13.90 | 17.90 | 27.00 | 9.30 | 15.00 |
| t ₄₀ (min) | 6.95 | 8.28 | 3.75 | 9.48 | 8.41 | 3.07 |
| t ₉₀ (min) | 31.75 | 13.47 | 26.67 | 31.88 | 14.68 | 10.67 |
| Processibility | | | | | | |
| Mooney viscosity | | | | | | |
| (lb-in) | 74.30 | 68.60 | 114.00 | 80.80 | 31.40 | 156.00 |
| t ₀₅ (min) | 15.20 | 35.60 | 6.13 | 8.53 | 10.53 | 1.20 |
| t ₃₅ (min) | 23.07 | 44.00 | - | 10.00 | 13.20 | 2.80 |
| Tensile property | | | | | | |
| Hardness (JIS A) | 60.0 | 58.0 | 56.0 | 70.0 | 71.0 | 62.0 |
| Modulus (kg/cm ²) | | | | | | |
| 100% | 13.5 | 19.3 | 18.8 | 16.2 | 35.1 | 24.6 |
| 300% | 33.5 | 66.5 | 80.0 | 48.1 | 126.9 | 142.7 |
| Tensile strength | | | | | | |
| (kg/cm ²) | 161.0 | 177.0 | 201.0 | 217.0 | 297.0 | 319.0 |
| Elongation (%) | 838.0 | 540.0 | 560.0 | 659.0 | 556.0 | 532.0 |

^a : solution-polymerized SBR

^b : natural rubber

° : N-GA(1.0)-SIL

【Effect of the Invention】

Silica according to the present invention considerably enhance the tensile strength and the elongation at break as a reinforcing material of rubber compounds to increase the elasticity of rubber compounds. According to this, silica is added to rubber compounds requiring high stability for impact and the thermal resistance and it contributes to not only enhance the lifetime and stability but also cut-down of energy and resources due to elongation of lifetime. Networked silica produced by coupling silica particles with carbon chains with proper length increases the physical properties, especially the tensile strength of rubber compounds. Rubber molecules in fluid state intrude into among silica and are entangled with silica particles to maximize the effect for enhancing the tensile strength. Moreover, heterogeneity of the physical properties caused by inorganic silica, which is immiscible with rubber compounds, can be completely solved. The surface of silica particles is covered with organic materials, carbon chains and the rubber molecules intrude into among silica particles so that the dispersion properties of the silica particles are maximized. Since curative accelerators or activators added to the rubber compounds were absorbed by polar functional groups on the surface of the silica, depending on increase in a loading amount of additives, the loading amount of additives increases to compensate for the loss of rubber additives. However, since polar functional groups on the surface of silica were already shielded by silane in networked silica, there is no need for increase in the loading mount of additives. Although non-reacted additives cause additional reactions, lower the physical properties of rubber compounds and result in environmental pollution by vaporizing at high temperature, the use of networked silica can contribute to cost cut down of the

rubber compounds and the environmental preservation because expensive additives such as curative accelerators don't have to be used excessively. Organic silane coupling reagents added for enhancing the dispersion property of silica and reinforcing effect generate ethanol during mixing and lower the Processibility. Moreover, when the mixing temperature is above 170 °C, bridge chains are dissociated and curing reaction is processed so that the mixing can not be sufficient for dispersion of silica. However, since in networked silica, silica particles are combined with one another by stable carbon chains during manufacturing process, networked silica is preferred in the aspect of no concern about generating harmful materials or dissociation.

【Claims】

【Claim 1】

A networked silica having three-dimensionally connected bridge chains among silica particles produced by introducing a functional group on the surface by a reaction of silanol groups on the surface of silica with alkoxyl silane having functional groups chosen from epoxy, amine, imine, halogen atoms, thiol and hydroxy groups and reacting that again or reacting a coupling reagent having diisocyanate, halogen atoms, or ester groups at both ends of carbon chain and silica.

【Claim 2】

A process for manufacturing a networked silica having three-dimensionally connected bridge chains among silica particles comprising introducing a functional group on the surface by a reaction of silanol groups on the surface of silica with alkoxyl silane having functional group chosen from epoxy, amine, imine, halogen atoms, thiol and hydroxy groups and reacting that again or reacting a coupling reagent having diisocyanate, halogen atoms, or ester groups at both ends of carbon chain and silica.

【Claim 3】

A process for manufacturing a networked silica as claimed in claim 3,

wherein 1-100g of the alkoxyl silane having functional group chosen from epoxy, amine, imine, halogen atoms, thiol and hydroxy groups are dissolved in a solvent such as toluene, xylene, octane, butanol at 1 °C to mix with silica, heated at 40-150 °C with refluxing to be combined primarily and silica coupled with silane are mixed and heated with refluxing at 40-150 °C to couple 0.05~2.0mmol of silane per g of silica.

【Claim 4】

A process for manufacturing a networked silica comprising dissociating 1~100g

of a coupling reagent having diisocyanate, halogen atoms and ester groups at both ends of hydrocarbon having 6~18 carbons in a solvent in claim 2 at 1 °C to mix with silica, heating with refluxing at 40~150 °C to couple 0.05~2.0mmol of silane per g of silica through one step.

【Claim 5】

A process for manufacturing a rubber composition of which tensile strength is reinforced by mixing 100phr of raw rubber compound, which is natural rubber, synthetic rubber such as styrene-butadiene rubber, butadiene rubber or its combination, with 5~100 by weight of a networked silica with zinc oxide, curative accelerator, activator, retarder.